CAA Inspection Report

CITGO Petroleum Corporation
Lemont Refinery
135th Street and New Avenue
Lemont, Illinois

Dates of Inspection:	June 7, 2010
Date of Draft Report:	July 26, 2010
Date of Final Report:	November 5, 2010
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11/5/2010
Date

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Inspection Report
CITGO Petroleum Corporation
Lemont Refinery
Lemont, Illinois

Prepared for:

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Air Enforcement Division
Office of Civil Enforcement
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5 November 2010

EPA Contract No. EP-W-09-033
Work Assignment ETS-0-2(CE)

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CITGO Petroleum Corporation
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135th Street and New Avenue
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3. BACKGROUND AND OBJECTIVES

EPA conducted an inspection of the CITGO Lemont Refinery (CITGO Lemont) in Lemont, Illinois from June 7 through June 11, 2010. EPA inspected equipment, reviewed documents, and interviewed plant personnel to determine compliance with applicable environmental statutes, regulations, rules, decrees, approvals, and permits under the Clean Air Act. Prior to the inspection, EPA notified CITGO Lemont of the inspection and provided an initial list of documents needed for review (Attachment A). CITGO Lemont provided some of these documents for EPA during the inspection and provided additional documents after the inspection. CITGO submitted their complete response, with exception of the coker data (Request 36), to EPA's Region 5 office on July 27, 2010. EPA returned to CITGO Lemont on September 21, 2010 to observe CITGO's turnaround inspection of the fluid catalytic cracking unit wet electrostatic precipitator.

During the inspection, EPA informed CITGO Lemont the reasons for the inspection were to evaluate compliance with the Clean Air Act, and particularly with CITGO's Consent Decree (CD) with EPA. This report describes the refining processes and operations at the CITGO Lemont refinery. Detailed descriptions are included for the following operations:

- Catalytic reformers;
- Fluid catalytic cracking unit;
- Alkylation unit;

- Ultra low sulfur diesel project;
- Delayed cokers;
- Sulfur recovery plant;
- Benzene storage and transport;
- Flares; and
- Wastewater treatment plant.

Several attachments are applicable to the entire report. Attachment A contains the pre-inspection notification and initial document request. Attachment B provides a plot plan and simplified process flow diagrams that CITGO Lemont provided and Attachment C contains photographs taken during the inspection.

4. FACILITY DESCRIPTION

The CITGO Lemont Refinery in Lemont, Illinois is owned by PDV America, Inc., an indirect, wholly owned subsidiary of Petróleos de Venezuela, S.A. (PDVSA), the national oil company of Venezuela. The original plant, now referred to as the North Plant, was constructed in the early 1920s and primarily produces petrochemicals. The newer South Plant was built around 1970, and comprises the main refinery units. CITGO Lemont processes approximately 167,000 barrels per day (bpd) of crude oil, mostly Canadian, into a variety of products including fuel gas, propane, solvents, gasoline, heavier fuels, petroleum coke, asphalt feedstock, and sulfur.

The CITGO Lemont Refinery is covered under the CITGO Consent Decree (No. H-04-3883, S.D. Texas, lodged on October 6, 2004 and entered on January 26, 2005). The CITGO Consent Decree includes affirmative relief projects to reduce emissions from the FCCU, heaters and boilers, sulfur recovery plants, hydrocarbon flaring, and acid gas flaring.

5. PROCESS OVERVIEW

Ms.Yvonne Jeanneret and other refinery personnel presented an overview of refining operations based on the process flow diagrams included in Attachment B.

CITGO Lemont operates a crude and vacuum unit (Units 111 and 217). In the crude unit, crude oil feed is first heated in exchangers and desalted. Desalter water is routed through the sour water stripper, then to wastewater treatment. The desalted crude oil is heated in two furnaces before distillation in a single column. The atmospheric distillation tower separates the crude oil into light gases, naphtha, distillates, and gas oils. Crude bottoms are further processed in the vacuum distillation unit, with one charge heater, into gas oil and vacuum tower bottoms.

Two semi-regenerative reformers catalytically upgrade low-octane-number medium and heavy naphtha from the crude unit. CRU 1 (Unit 123) produces benzene-rich reformate for the CITGO Lemont petrochemicals plant (North Plant). CRU 2 (Unit 116) produces reformate for gasoline blending in the refinery (South Plant). Section 6 discusses the catalytic reformers in greater detail.

The fluid catalytic cracking unit (FCCU, Unit 112) processes gas oils from the crude and vacuum distillation units. The FCCU has a partial-burn regenerator and uses a CO boiler to complete combustion to CO_2. CITGO Lemont uses a selective catalytic reduction (SCR) system for NO_X control and a flue gas scrubber with a wet electrostatic precipitator (WESP) to remove SO_2 and particulate matter. Section 7 discusses the FCCU in greater detail.

CITGO Lemont has a hydrofluoric acid (HF) alkylation unit (Alky, Unit 120) that processes feed from the FCCU to form high-octane-number alkylate for gasoline blending. Section 8 discusses the Alky in greater detail.

CITGO Lemont was issued a construction permit on June 16, 2008 for various changes to the refinery in order to produce ultra low sulfur diesel (ULSD). The ULSD hydrotreater (Unit 590) and associated equipment are scheduled to begin operating in July 2010. During the inspection, CITGO provided further explanation of the changes and tie-ins which have taken place during the project. Section 9 discusses the ULSD project in greater detail.

Two delayed coking units (cokers) thermally crack vacuum tower bottoms, or resid, to produce naphtha and gas oils, along with light gases, C_4s, and petroleum coke. Coker 1 (Unit 113) currently produces sponge coke. Coker 2 (Unit 108) originally produced needle coke and was modified to produce sponge coke, but it has been shut down since August 2009 for economic reasons. Section 10 discusses the cokers in greater detail.

Several process units generate light gas streams that contain hydrogen sulfide (H_2S). CITGO Lemont uses multiple amine contactors throughout the refinery to absorb H_2S from the hydrocarbons, producing refinery fuel gas (RFG). The H_2S is subsequently removed from the amine solutions and converted to elemental sulfur at the sulfur recovery plant (SRP, Units 119 and 121). Sour water stripper (SWS) gas generated by four strippers is also treated at the SRP. Section 11 discusses the SRP in greater detail.

CITGO Lemont has five flares: the North Plant Flare, two South Plant Flares, the Coker 2 Flare, and the Alky Flare. All flare systems except the Alky Flare include flare gas recovery (FGR). Section 12 discusses the flare gas system in more detail.

CITGO Lemont treats process water from the North and South Plants in a common wastewater treatment plant (WWTP). Section 13 discusses the WWTP in more detail.

6. REFORMERS

CITGO Lemont has two reformers, CRU 1 and CRU 2, that catalytically upgrade naphtha. CRU 1 is used for petrochemicals production, and CRU 2 reformate is used in gasoline blending. Ms. Yvonne Jeanneret provided information on the reformers during the introductory presentation on June 7. In addition, Mr. David Van Dyke and other refinery personnel responded to questions from EPA regarding the regeneration operation. Attachment B provides process flow diagrams for the reformers (pp. 5–6), and Attachment C provides pictures taken during the tour (Photograph 58).

6.1 CRU 1 Process Description

CRU 1 (Unit 123) is part of CITGO Lemont's North Plant petrochemicals complex. CRU 1 started up in 1957, and currently processes [redacted] bpd of medium straight run naphtha. Final liquid product, or reformate, contains 10 to 15 percent benzene and is used as feed for aromatics and solvent production. CRU 1 includes two heaters in the hydrotreating section and three heaters in the reforming section, none of which currently have emissions controls or NO_X CEMS. The largest of the five heaters, 123B-2, will be equipped with NO_X CEMS in the next year and a half due to Illinois EPA RACT requirements. CRU 1 has three reactors filled with a Criterion reforming catalyst. Because the reforming reactions are endothermic, the feed is reheated between each reactor.

6.2 CRU 2 Process Description

CRU 2 (Unit 116) started up in 1970. CRU 2 currently processes [redacted] bpd of feedstock comprising heavy straight run and heavy coker naphthas that have been hydrotreated in the Unit 114 naphtha desulfurizer. CRU 2 has three spherical reactors, each with an associated heater, and a fourth heater serves as the stabilizer reboiler. The burners in the two largest heaters will be retrofit next spring with ultra low NO_X burners. CRU 2 uses a UOP R-56 catalyst to convert feed paraffins and naphthenes into aromatics.

A product separator vessel splits a hydrogen-rich gas stream from the liquid products. The hydrogen is compressed and recycled to the beginning of the reforming process. The liquid products from the separator continue to a stabilizer column. Stabilizer column overheads are treated at the Saturated Gas Plant. The reformate is used in gasoline blending.

6.3 Catalyst Regeneration

Over time, coke deposits on the reforming catalyst and catalytic sites are deactivated. The reforming catalyst must be periodically regenerated by combusting the coke and chemically reactivating the catalytic sites. The CRU 1 catalyst is regenerated every four to five years while the CRU 2 catalyst is regenerated every one to two years. Both units are semi-regenerative reformers, meaning the unit is brought down for regeneration, and the catalyst in all reactors is regenerated at the same time.

The regeneration cycle includes several phases to remove coke and rejuvenate the catalytic sites. First, air diluted with nitrogen is heated and injected before the first reactor and between the third heater and reactor. The temperature and oxygen concentration are controlled to maintain a slow coke burn to avoid damaging the catalyst. A maximum temperature of [redacted]°F is targeted. [redacted] is added to maintain a specific water-to-chloride ratio. During the second step, or "proof burn," the oxygen content of the air is increased to two percent and the temperature is increased to ensure all coke is burned.

After the coke is burned off the catalyst, the catalyst is normally then rejuvenated in the oxychlorination step. The temperature is increased to [redacted]°F and the oxygen content is increased to five percent. CITGO Lemont adds perc as a chloriding agent to redisperse the active catalyst sites and form acid chloride sites. The oxychlorination step lasts for [redacted] hours. Afterwards, a mixture of nitrogen and hydrogen is circulated through the reactors to reduce the metal sites from their oxide states. Next, SulfrZol sulfiding agent is circulated through the reactors to slightly poison the catalyst, removing hyperactivity which could result in a large exotherm when hydrocarbons are reintroduced to the unit.

During regeneration, the effluent gas from the reactors is largely nitrogen and is recirculated in the process. This regeneration gas is scrubbed after each pass to remove HCl from the regeneration gas before returning to the reactor. Temporary equipment is brought in for CRU 1 regenerations. For CRU 2, the product separator vessel serves as the scrubber, with water injected through quills in the piping upstream of the vessel. While most of the regeneration gas from the scrubber is recirculated, a portion is bled off for pressure control and emitted to the atmosphere through a vent. EPA asked CITGO whether the scrubber water has ever been tested for dioxin; it has not.

The most recent CRU 2 regeneration prior to EPA's June 2010 inspection was in November 2008. During this regeneration, the catalyst was also replaced after a greater than 10 year run. Therefore, the coke was burned off the old catalyst without perc addition and there was no oxychlorination step.

7. FLUID CATALYTIC CRACKING UNIT

CITGO Lemont has one FCCU with a nominal capacity of [redacted] bpd. Mr. Paul Case provided information on the FCCU during the introductory presentation on June 7. In addition, Mr. Phil Pribnow and Mr. Dennis Willig led a tour of the FCCU on June 8. EPA also interviewed Mr. Gary Ephraim and Mr. Matt Cordina on June 10, regarding projects for the FCCU regenerator cyclones, slide valve, orifice chamber, and stripper, and WESP downtime. Attachment B provides process flow diagrams for the FCCU (p. 2) and Attachment C provides pictures taken during the tour of the FCCU (Photographs 38–39, 42–47, 50–51, 53–57, 73–76, 78, 80–84, 90).

7.1 FCCU Process Description

CITGO Lemont's FCCU is a UOP-designed side-by-side unit and started up in 1970. It processes up to [redacted] bpd of feed mainly unhydrotreated atmospheric, vacuum, and coker gas oils. Since the idling of Coker 2, its hydrotreater has been repurposed to hydrotreat FCCU decant oil for reprocessing in the FCCU. The combined feed is preheated and injected into a vertical riser, contacts the circulating catalyst powder over the span of a few seconds, and is converted into lighter hydrocarbons while some of the feed forms coke on the catalyst.

The hydrocarbon vapors and spent catalyst exit the riser into a reactor vessel. The reactor is controlled to a temperature of [redacted]°F. Primary and secondary cyclones within the reactor separate the hydrocarbon vapors from the spent catalyst. Additional light hydrocarbons are recovered by steam stripping the spent catalyst at the bottom of the reactor. Hydrocarbon vapors flow through an overhead line to the fractionator which separates the vapors into various product streams

The spent catalyst flows from the stripper to the regenerator. The FCCU regenerator operates in partial burn, meaning oxygen availability limits combustion, so that coke burning produces significant amounts of both CO and CO_2. The spent catalyst has approximately 0.2 to 0.3 weight percent carbon. To verify the catalyst carbon content, refinery personnel may take catalyst samples from the regenerator for visual comparison against vials containing catalyst with various known carbon contents. Nickel and vanadium content on spent catalyst are also monitored due to conversion concerns. CITGO injects up to [redacted] gallons per hour of antimony, to act as a nickel passivator. CITGO targets [redacted] ppm nickel and [redacted] ppm vanadium content on spent catalyst. Spent catalyst is stored in a hopper and trucked off-site on a regular basis. CITGO adds 6 to 15 tons per day of fresh catalyst to the regenerator.

Regenerator flue gas passes through seven sets of primary and secondary cyclones to disengage catalyst particles. The flue gas then enters the CO boiler. In the CO boiler, combustion to CO_2 is completed and waste heat from the flue gas is recovered to generate steam. Flue gas from the CO boiler is routed to a selective catalytic reduction system (SCR) for NO_X removal. In the SCR, NO_X and ammonia adsorb on the surface of a tungsten and vanadium catalyst where they react to form molecular nitrogen and water. From the SCR, the flue gas enters a Lurgi wet gas scrubber (WGS) equipped with a wet electrostatic precipitator (WESP) for SO_2 and PM removal. The WESP is the wider section of the scrubber tower in Photographs 51 and 53. The WGS/WESP originally came online in December 2007, but the WESP had not been operational for an uncertain length of time preceding the inspection, according to refinery personnel. Scrubber blowdown is routed to a purge treatment unit (PTU) for removal of catalyst fines. The effluent from the PTU is sent to the treated water basin without further processing in the wastewater treatment plant.

The flue gas is then exhausted through a stack equipped with CEMS for SO_2, NO_X, CO, and O_2. According to refinery personnel, SO_2 emissions are typically less than 25 ppm, NO_X emissions are usually 15 to 18 ppm, and PM is usually well below 0.5 pounds per thousand pounds of coke burn. During the plant tour on June 8, Haney Stevenson stated that the O_2 analyzer was currently plugged with salts and not operational. In response, CITGO hired a contractor with a temporary diagnostics truck to monitor emissions. EPA observed CEMS readout in the diagnostics truck showing emissions of 82.7 ppm NO_X, 13.12 ppm CO, and 1.5% O_2.

7.2 FCCU WESP Issues

Per the CITGO consent decree with EPA, CITGO Lemont installed a WGS and accepted the following FCCU SO_2 limits, effective December 31, 2007:

- 25 ppmvd SO_2 at 0% O_2 on a 365-day rolling average basis; and
- 50 ppmvd SO_2 at 0% O_2 on a 7-day rolling average basis.

CITGO Lemont elected to install a Lurgi WGS which included a WESP for removal of remaining particulate and sulfuric acid mist from the regenerator flue gas. Previously, the FCCU had been equipped with two ESPs on the CO boiler outlet, which emitted through a combined stack. The current WGS/WESP system started up in December 2007.

CITGO personnel were uncertain as to when exactly the WESP stopped operating. According to a CITGO control room FCCU supervisor, this event occurred approximately one and one-half years prior to the June 2010 EPA inspection. At EPA's request, CITGO is currently looking at historical trend data to provide EPA a better approximation of the WESP shutdown time frame. After extensive troubleshooting, CITGO Lemont hypothesized that the cause of WESP failure was one or more wash nozzles becoming unattached and falling onto the WESP grid, causing an electrical short.

EPA expressed concern over PM emissions during the time period the WESP was not operating. CITGO stated during the EPA inspection that they plan to conduct a stack test on the FCCU in late June. On June 30, 2010 and July 1, 2010, CITGO conducted testing for PM emissions from the FCCU WESP stack using EPA Method 5B/202 and provided the source test report to EPA. The report shows average front-half PM emissions of 1.18 lb/mlb of coke burn, compared to an allowable emission rate of ≤1.0 lb/mlb of coke burn. This test report is included in Attachment F.

During the FCCU turnaround conducted during September 2010, CITGO repaired the WESP and returned it to operation. EPA personnel returned to the refinery on September 21, 2010 to observe CITGO's turnaround inspection of the WESP. Mr. Gary Ephraim provided a chain of CITGO email communication and photographs taken during the inspection of the WESP. According to the email communication, CITGO concluded during the turnaround inspection of the WESP that the stud bolt holding one of the electrodes had broken, and the electrode had dropped through the grid onto the distribution tray. The email communication also stated: "A large number of stud bolts on the east side of the WESP were found to be loose and not tightened. This connection consists of a set of washers and nuts fastening the stud to the buss grid and another set of nuts holding the electrode. Most of the washers were either very thin or missing, allowing the nuts to come loose and the stud connection to move (wiggle)." CITGO also inspected the WGS and noted potential issues to address. Attachment G provides the chain of email communication regarding the WESP/WGS turnaround inspection, and Attachment H provides the photographs taken by CITGO during the WESP turnaround inspection.

7.3 <u>2010 FCCU Turnaround Projects</u>

During the plant tour on June 8, refinery personnel providing the FCCU overview described an upcoming project to replace the FCCU regenerator head and cyclone system during the upcoming fall 2010 turnaround. The support structure for construction of the new regenerator head is shown in Photograph 50. The new regenerator cyclones are shown in Photograph 90. Attachment I provides photographs taken by CITGO during the fall turnaround that show the FCCU regenerator head being lifted for replacement. On March 18, EPA interviewed Mr. Gary Ephraim and Mr. Matt Cordina regarding these FCCU projects. Mr. Ephraim stated that the current FCCU regenerator cyclones, slide valve, and orifice chamber are all at the end of their useful life due to metallurgical degradation. The current regenerator is approximately [redacted] feet in diameter and contains [redacted] pairs of cyclones. After considering several options for replacement, CITGO Lemont decided to remove the regenerator top head and replace it with a pre-fabricated head and [redacted] new pairs of cyclones. CITGO Lemont is aiming to improve regenerator reliability and achieve a [redacted]-year life with cyclones that are both longer and wider in barrel diameter. The length of the cyclones will increase by approximately [redacted] feet. The barrel diameter will increase from [redacted] inches to [redacted] inches on primary cyclones, and from [redacted] inches to [redacted] inches on secondary cyclones.

The most recent, and only, regenerator cyclone replacement was in 1989. In addressing the design basis for the new cyclones, Mr. Cordina stated that the previous cyclones were sized for [redacted] bpd, which was undersized in terms of reliability. CITGO has looked at recent historical throughput data and sized the new cyclones based on a maximum expected throughput of approximately [redacted] bpd. The total potential amount of feed entering the reactor riser is limited to [redacted] bpd, based on fractionator overhead relief valve capacity.

According to Mr. Cordina, the current primary constraint on FCCU capacity is the air blower, which will remain unchanged during this project. However, Mr. Cordina was unsure how the project's effect of decreased cyclone pressure drop would be addressed to maintain the overall pressure balance between the FCCU reactor and regenerator. EPA requested documentation showing the incremental pressure drop change due to the cyclone replacement project.

Other FCCU projects planned for the fall 2010 turnaround include replacing the FCCU flue gas slide valve and orifice chamber, which are at the end of life. Refinery personnel indicated the replacement equipment are close to like-in-kind equipment. The port size on the slide valve will be decreased and the metallurgy of the orifice chamber will be changed. The slide valve and orifice chamber are being sized based on regenerator pressure. The slide valve operating pressure will decrease, and orifice chamber pressure will increase, to maintain constant regenerator pressure. CITGO Lemont commissioned a [redacted] study for the slide valve/orifice chamber system, which will be provided to EPA for review.

EPA also addressed an AFE for improving the FCCU stripper. CITGO Lemont's stated objective was to improve stripping efficiency, and improve yields, [redacted]. The AFE states that this project is "compatible with and designed for future feed quality decreases." CITGO stated that this lower quality feed refers to heavier feed to the FCCU, but does not include vacuum tower bottoms; the worst quality expected feed would be hydrotreated decant oil.

8. Alkylation Unit

CITGO Lemont's hydrofluoric (HF) acid alkylation unit (Alky) started up in 1984. The Alky currently processes [redacted] bpd feed to form high-octane alkylate for gasoline blending. The FCCU uses a [redacted]-maximizing additive to provide the Alky with olefin-rich feed. Ms. Yvonne Jeanneret and other refinery personnel discussed the Alky and its associated safety systems during the introductory presentation on June 7. Attachment B provides process flow diagrams for the FCCU (p. 3).

CITGO Lemont has a Rapid Acid Deinventory (RADI) system to prevent the release of HF acid in the event of an emergency requiring evacuation of the reactor vessel. The system would allow the HF acid inventory from the Alky vessel to be dumped into an emergency receiving tank. A water curtain designed to provide a 40-to-1 water-to-HF acid ratio surrounds the area and would be used to contain escaped HF acid vapor. The curtain is designed for 35,000 gallons per minute flow, supplied by a spring-fed freshwater lake across the street from the refinery. Additional controls in place include a deluge system around likely leaks which is supplied by refinery fire water, 10 remote-controlled water cannons, 44 HF acid and hydrocarbon sensors throughout the Alky, and a video camera for remote monitoring. CITGO Lemont tests the water curtain at full flow twice per year. Individual components of the RADI system are tested once per month. The RADI software is tested during every turnaround, approximately every [redacted] years. The next scheduled Alky turnaround is in September 2010.

9. ULTRA LOW SULFUR DIESEL PROJECT

CITGO Lemont was issued a construction permit on June 16, 2008 for various changes to the refinery in order to produce ultra low sulfur diesel (ULSD). The most recent revision of the permit was issued on April 21, 2010. The ULSD hydrotreater (HT) is scheduled to start up in July 2010. During the inspection, CITGO provided further explanation of the changes and tie-ins which have taken place during the project. During the plant tour on June 10, EPA viewed new and affected units. Also on June 10, EPA interviewed Mr. Mike Hammond and Mr. Don Graffy regarding the ULSD project. Attachment C provides photographs of the new and affected units taken during the tour (Photographs 96–112).

9.1 ULSD Project Description

The new ULSDHT includes a reactor charge heater and stripper reboiler heater, each equipped with John Zink COOLstar-15M round flame ultra low NO_X burners. The reactor vessel has [redacted] catalyst beds and will operate at approximately [redacted] psi.

Two existing hydrotreaters, the Light Distillate Hydrotreater (LDHT, Unit 115) and the Diesel Distillate Hydrotreater (DDHT, Unit 125) formerly exchanged heat with streams exiting the crude unit. Piping has been reconfigured so that the DDHT will feed the ULSDHT, and product from the LDHT will be blended with ULSDHT product. The DDHT will therefore be run at lower severity than previously. The LDHT reactor, which held [redacted] pounds of catalyst, was replaced with a larger reactor which will hold [redacted] pounds of catalyst. Two existing heaters in the LDHT are included in the construction permit as affected units, due to piping changes. The stripper reboiler heater exit piping has been modified.

Sulfur recovery Trains C and D were modified to handle additional sulfur feed. The front end burner on Trains C and D was modified to accommodate increased oxygen enrichment capability (discussed in Section 11). The new hydrogen plant required to supply the ULSDHT is owned and operated by Linde. The plant is built on land leased from CITGO. This plant will be dedicated to production of hydrogen for CITGO's ULSDHT. New and modified units are tied in to the South Plant Flares (C-2 and C-3) system. A unit header on the ULSDHT collects all vents and connects to the flare system header.

9.2 ULSD Project Permitting

The CITGO consent decree (CD) with EPA requires that, for CD emissions reductions to be used as credits or offsets in permitting, a federally enforceable, non-Title V Permit must contain limits for heaters and boilers of 0.020 lb NO_X per MMBTU or less on a three-hour rolling average basis..CITGO's April 21, 2010 construction permit presents short-term limits of 0.04 lb NO_X per MMBTU for the new heaters and 0.0980 lb NO_X per MMBTU for the modified existing heaters. The CITGO CD also restricts the NO_X CD emission reductions used as credits or offsets to 300 tons per year across all of CITGO, not just at CITGO Lemont. The ULSD construction permit uses all 300 tons per year of NO_X for this project.

The two new ULSDHT heaters, 590H-1 and 590H-2, have a maximum fired duty of 67.5 and 64.9 MMBTU per hour, respectively. According to CITGO Lemont, John Zink provided guaranteed emissions for both new heaters based on firing CITGO Lemont's refinery fuel gas: 0.35 lb NO_X per MMBTU; 100 ppmvd CO; 3.64 lb VOC per MMscf; and 9.17 lb PM per MMscf. These new heaters do not have NO_X CEMS.

Due to project tie-ins to the South Plant Flares system, the C-2 and C-3 flares will become subject to requirements under NSPS Subpart Ja. CITGO stated that they are aware of this applicability and are awaiting promulgation of the final rule to determine the method and schedule for compliance.

10. DELAYED COKERS

CITGO Lemont has two delayed cokers. Coker 1 has a nominal capacity of [redacted] bpd and Coker 2 has a nominal capacity of [redacted] bpd. Coker 2 was not operating at the time of EPA's inspection. Mr. Phil Pribnow and Mr. Dennis Willig led a tour of Coker 1 on June 9. EPA also interviewed Mr. Pribnow and Mr. Willig about the cokers on June 10. Attachment B provides process flow diagrams for the coker (pp. 4, 14) and Attachment C provides photographs of Coker 1 taken during the tour (Photographs 24, 59–72).

10.1 Coker 1 Process Description

CITGO Lemont's Coker 1 started up in 1970, and currently processes approximately [redacted] bpd of vacuum tower bottoms (VTB) into sponge coke. Coker 1 has three heaters and six drums. The first four drums were installed as part of the original coker in 1969, while the fifth and sixth drums were installed in 1985. The coke drums operate in pairs, with a dedicated heater for each pair. The VTB is flashed in the bottom of the coker's combination column before being pumped to the charge heaters. The VTB is heated and then flows into the drums where thermal cracking occurs. The unit is designed so that the majority of reactions occur in the coke drums rather than the heaters, thus the term "delayed coking." Hydrocarbon vapors produced by the cracking reactions flow through overhead lines to the combination column for separation into light and heavy coker gas oil (LCGO and HCGO, respectively), naphtha, and wet gas. The remaining material solidifies to form coke.

When a drum fills with coke, the feed is redirected to its paired drum, and steam is injected to strip volatile hydrocarbons from the coke in the full drum. During steaming, the drum is vented to the combination column for 30 minutes and then vented to the "steam out" (blowdown) line for 30 minutes. After steaming, the coke is water-quenched for approximately four hours, during which water level is 15 feet above the coke, then allowed to soak for an additional hour. Waste streams including sludge from tank bottoms and from cleanings of process tanks may also be introduced to the coke drum at this point. The drum pressure is drawn down to less than 5 psig, at which point the drum is vented to atmosphere and the quench water is drained from the drum. The drum is then deheaded and the coke is hydraulically cut from the drum.

The coker steam out lines are routed to a steam out system which condenses and separates heavy hydrocarbons from lighter hydrocarbon and water vapors. Recovered oil is sent for further processing, and sour water is sent for stripping in Unit 119. Solid coke cut from drums is discharged into an adjacent pit. Cranes pick up the coke and drop it into piles. Oxbow transports the coke off site, either to a calciner facility or onto a barge.

Filling the drum with coke takes about [redacted] hours, and the full cycle takes [redacted] hours. The six drums share certain assets, including the steam out system and cutting water jet pump; therefore, the cycles of each drum pair are staggered. Attachment D contains information provided to EPA during the inspection on Coker 1 cycle time changes since 1985.

During the plant tour on June 9, at 1:30 p.m., EPA observed real-time coker process data from the control room. Drum 4 of Coker 1 was scheduled to begin venting at approximately 2:00 p.m. that afternoon. The drum pressure and temperature at 1:30 p.m. were [redacted] psig and [redacted]°F. According to Mr. Ed Perry who was monitoring Coker 1 from the control room, a drum pressure below 5 psig and temperature below [redacted]°F indicate that a drum is ready to vent. Mr. Perry stated that this rule of thumb has been in place for approximately 20 years. At approximately 2:20 p.m., operators on site at Coker 1 announced that the current Drum 4 pressure was 2.4 psig and the temperature was [redacted]°F. Seconds later, EPA observed Drum 4 venting to the atmosphere (see Photographs 67–72). The coker unit supervisor stated that while the vent is open, the quench water soaks for approximately one hour, followed by draining for one hour. He stated that during this time period, the visible steam flow dissipates, and is no longer visible after approximately one and one-half hours.

10.2 Coker 2 Process Description

CITGO Lemont's Coker 2 started up in 1983, and has a capacity of [redacted] bpd. Originally, Coker 2 produced needle coke from VTB. In September 2005, the coker switched to producing sponge coke from VTB. Since August 2009, Coker 2 has been shut down due to low coking margins. At the refinery's current rates, there is not enough VTB to operate both cokers... Most recently, filling a drum with coke took about [redacted] hours, and the full cycle took [redacted] hours. Similar to Coker 1, Coker 2 drums share certain assets, including the steam out system and cutting water jet pump; therefore, the cycles of each drum pair are staggered. Attachment D contains information provided to EPA during the inspection on Coker 2 cycle time changes since 1985.

10.3 <u>Coker Projects</u>

On June 10, EPA interviewed Mr. Pribnow and Mr. Willig about changes to Coker 1 which have led to shorter cycle times and thus an increase in the drum cycles per day. EPA asked whether any cycle time changes required physical work to the coker. CITGO explained that tools have changed over the years; for example, cutting water is more focused and effective. The jet pump which supplies cutting water has not been modified in the last 15 years; unit personnel mentioned during the plant tour that nozzles may have been replaced in the 1980s. CITGO also explained that when the unit was designed, it included built-in relief capacity. Around 1998, an additional flare header was installed for relief capacity which allowed increased coker rates. Other small projects also facilitated the cycle time changes. Since 2000, there has been only one coker turnaround. During the 2002 turnaround, work was done on compressor cooling, fractionator overhead cooling, relief valves, and the DeltaValve unheading system.

EPA also asked about the status of specific recent coker-related AFEs. CITGO personnel stated that replacing all six Coker 1 drums per project number P.105511 "Replace Coker 1 Coke Drums" AFE (July 31, 2007) will be conducted during the next turnaround. Three of the new coke drums are shown in Photograph 91. The Coker 1 drums are original and date from 1969 (drums 1 through 4) and 1985 (drums 5 and 6). Also during the next turnaround, CITGO will conduct work on the coker fractionator per project number P.106497 AFE "Debottleneck Coker 1 Fractionation" (November 10, 2008). The [redacted] will be replaced. The [redacted] replacement will improve cutpoints of HCGO, LCGO, and naphtha. The tower currently runs in and out of overflow conditions; work during the upcoming turnaround will allow the tower to handle a higher rate. However, other limiting factors exist. Currently, Coker 1 is limited by issues such as need to control foam rise in the coke drums. Regarding the AFE text addressing increasing VTB processing at Coker 1, CITGO personnel stated that this idea is still in deliberation.

Refinery personnel stated that a decision had not been made whether to pursue a project based on project number P.106647 "Improve Coker 1 Compressor Reliability" AFE (August 15, 2008) for a study on how to increase the run length of the Coker 1 compressor from [redacted] years to [redacted] years.

11. SULFUR RECOVERY PLANT

CITGO Lemont has four Claus sulfur recovery units, identified as Trains A through D. Trains A and B share a Flexsorb tail gas unit (TGU) and comprise Unit 119; Trains C and D have Beavon Stretford TGUs that share some components and comprise Unit 121. Mr. Phil Pribnow and Mr. Dennis Willig led a tour of Units 119 and 121 on June 8. Attachment B provides process flow diagrams for the sulfur recovery units (pp. 7–11), and Attachment C includes photographs taken during the tour (Photographs 1–15, 27–31, 33–37).

11.1 SRP Process Description

Unit 119 originally started up in 1970, and Unit 121 started up in 1976. The current total sulfur recovery plant capacity is approximately [redacted] long tons per day (ltpd). Trains A and B have a capacity of approximately [redacted] ltpd each, and Trains C and D have a capacity of approximately [redacted] ltpd each. Acid gas is produced in four amine regeneration units. CITGO Lemont currently uses monoethanolamine (MEA) for regeneration, but plans to convert to using methyldiethanolamine (MDEA) in June 2010, for energy savings. Acid gas from the amine regeneration units and sour water stripper (SWS) gas from four strippers are routed to the sulfur recovery units via combined headers for Trains A and B, and for Trains C and D. In the Claus process on each train, a portion of the H_2S is combusted to SO_2 at an approximate ratio of two-to-one (H_2S:SO_2), and then the H_2S and SO_2 are catalytically reacted to form sulfur and water.

The condensed sulfur is collected in a pit associated with each train. CITGO Lemont routes the pit vapors to the sulfur recovery unit incinerators via steam-jacketed 14-inch lines. Air enters the pits through intake stacks and is swept through by steam eductors. The sweep gas is then injected into the incinerator. The incinerator stacks are monitored for SO_2. The C and D incinerators also have H_2S analyzers, refinery personnel stated they are not currently used and may not be regularly maintained. During an interview with Mr. Matt Cordina on June 10, EPA noted a concern that H_2S or other reduced sulfur species might not be combusted to SO_2 if they are not introduced in the flame zone. Mr. Cordina stated that CITGO Lemont believes that a temperature of 875°F is needed to achieve 10 ppm H_2S, and the incinerators operate at approximately 1,050°F, as measured by a temperature indicator in the stack.

Tail gas from Trains A and B is treated in a tail gas unit equipped with an ExxonMobil Flexsorb absorber. This unit was added in late December 2008 to address CITGO Consent Decree requirements. The TGU catalytically reacts tail gas sulfur species, including SO_2 and reduced species such as carbonyl sulfide and carbon disulfide, to form H_2S. The reactor effluent is quenched and then the H_2S is absorbed by a proprietary ExxonMobil amine solvent. H_2S-rich amine from the TGU is analyzed daily for heat stable salts and H_2S content, then regenerated, and the stripped H_2S is recycled to the Claus units. The combined TGU vapor stream is then split between the two incinerators for Trains A and B. The injection point of the TGU vapors is above that for the pit vapors.

Tail gas from Trains C and D is treated in a Beavon Sulfur Removal TGU which uses a proprietary Stretford solution to absorb H_2S. Rather than an amine regenerator, the spent Stretford solution is treated in a series of three flotation tanks for oxidation. This TGU system has been in place since original construction of Unit 121. Trains C and D also have oxygen enrichment capability. As part of the ongoing ULSD project, CITGO Lemont plans to upgrade oxygen enrichment capability on the C and D trains from [redacted] percent oxygen. The incinerator for Trains C and D is stacked on top of the absorber, with a single burner at the narrowing interface between the two chambers. Consequently, the injection points of the pit vent and TGU vapors into the burner zone are relatively high above grade.

11.2 Steam Eductor Issues on Trains C and D

During the tour on June 8, CITGO Lemont personnel explained that there had been problems with the operation of the steam eductor systems for Trains C and D. EPA interviewed Mr. Matt Cordina regarding these issues on June 10. According to Mr. Cordina, the eductor systems for all four trains were designed at the same time, and one common minimum air rate that would be appropriate for all sulfur pits was applied. Therefore, the eductor systems for Trains A and B are the same approximate size as for Trains C and D, though these units handle less than half the sulfur load. The refinery is concerned with evidence of low air flow through the sulfur pits on Trains C and D, and plugging in the pit vapor lines caused by liquid sulfur. Recently, a drain valve was installed in the pit vapor line leading to the incinerator for Train C. CITGO Lemont plans to install a similar drain valve for Train D during the Fall 2010 turnaround. The most recent turnarounds on Trains C and D were 2008 and 2006, respectively. During these turnarounds, the steam eductor were shut down, and the sulfur pits were pumped dry to allow entry for maintenance.

Also during the tour on June 8, EPA noticed that the rain hat on the air intake for Train C was missing, as shown in Photographs 33 and 34. Refinery personnel were aware of the issue, but unsure how long the component had been missing. EPA also noticed a green/yellow residue surrounding the top of the air intake piping for Train D, shown in Photographs 30 and 31.

11.3 SRP Emissions

During the plant tour on June 8, EPA observed H_2S and SO_2 readings for the Train D incinerator on an instrument in the CEMS shed. The H_2S reading was approximately 6 ppm, and the SO_2 reading was approximately [redacted] ppm. EPA indicated that this may imply that approximately 10 percent of the reduced sulfur is not being combusted to SO_2. During the EPA interview, Mr. Cordina explained that the Train C and D incinerator stacks have H_2S analyzers that are not maintained or used. The CEMS on these stacks undergo daily calibration, but Mr. Cordina is unsure whether the H_2S analyzer is affected by this activity.

Based on emission data reviewed by EPA during the inspection, Trains A and B showed relatively high CO emissions in recent years. In years 2005, 2007, and 2008, CO emissions exceeded the Title V permit limit. Mr. Cordina stated that sources of CO may include fuel gas to the incinerator pilot burner, hydrocarbon present in acid gas, or the RGG unit which was installed in December 2007. At EPA's request, CITGO is currently in the process of preparing a formal response meant to explain the reason for the elevated CO emissions.

12. BENZENE STORAGE AND TRANSPORT

Benzene produced by CRU 1 in the North Plant is separated in the UDEX unit, then stored in tanks. During the plant tour on June 10, EPA observed Mr. Dave Cotter collecting a benzene sample from Tank 611, which contains benzene sales product. On June 11, EPA observed vacuum trucks which transport benzene-containing waste from CITGO Lemont's laboratory. Attachment C includes photographs taken during these activities (Photographs 113–120).

Benzene storage tank 611 has an internal floating roof. A sample tap is located approximately four feet above grade, on the side of the tank. On June 10, Mr. Cotter demonstrated a mock sample being taken from the tap, using two clear rubber-coated bottles. Mr. Cotter explained that the sample method begins with purging one quart of benzene into Bottle 1. Next, a one-quart sample is collected in Bottle 2. During collection into the bottles, the bottle being filled is held so that it encases the end of the sample tap. After the benzene is collected, the tap is closed and allowed to drip into the bottle. The bottles are then capped. Mr. Cotter believed that the purge sample is ultimately dumped into benzene waste collection.

EPA observed two vacuum trucks, Trucks 470 and 7294 which are used to transport benzene-containing laboratory waste. This waste is emptied from the laboratory twice per day into collection drums which are enclosed in a plastic, hard-shell container on the back loading dock of the building. A minimum of once per week, empty drums are swapped for the full drums. Each vacuum truck has a wand attachment which is used to suction waste from the full drums. Trucks 470 and 7294 are the primary trucks used for this purpose, and are used interchangeably. From the laboratory, the truck transports the waste directly to Tank 434. According to CITGO, neither of these trucks is equipped with filtration on the vent.

13. Flare Gas System

CITGO Lemont has five elevated flares. In addition, an enclosed vapor combustion device controls the fuels transport loading rack and is sometimes referred to as a flare. Refinery personnel provided an overview of the flares during the introductory presentation on June 7. Mr. John Martens led a tour of the Alky Flare and C-2 Flare on June 9. Attachment B provides process flow diagrams for the flares (pp. 12–14), and Attachment C includes photographs taken during the tour (Photographs 16–23, 25–26, 32, 48–49, 77, 79, 85–87, 92–95).

13.1 Flare Gas System Process Description

Table 12-1 lists the flares at the refinery, the process units that vent to each flare, any flare gas recovery (FGR) serving the flare, and the flare photographs in Attachment C.

Table 12-1. Flare Characteristics

Flare	Date Installed	Processes Routed to Flare	Flare Gas Recovery	Photograph Nos.
North Plant Flare, C-1	1968/1982 (FGR)	• Petrochemicals	Dedicated FGR system	
South Plant Block 2 Flare, C-2	1968/1982 (FGR)	• Refinery Block 2 units—including the FCCU	South Refinery Flare Gas Recovery System	16–21, 25–26, 32, 77, 79, 89, 92–95
South Plant Block 3 Flare, C-3	1968/1982 (FGR)	• Refinery Block 3 units—including the Crude Distillation Unit and Coker 1		

Table 12-1. Flare Characteristics

Flare	Date Installed	Processes Routed to Flare	Flare Gas Recovery	Photograph Nos.
Coker 2 Flare (C-4)	1985	• Coker 2 (Needle Coker Unit, not currently in service) • Hydrogen Plant	Dedicated FGR system	22–23
Alky Flare (C-5)		• HF Alkylation Unit	None	48–49, 85–87

The North Plant Flare, C-1 serves CITGO Lemont's petrochemical process units area. It has used steam injection for smokeless operation since 1990. Process units which vent to this flare are also served by a dedicated FGR system. CITGO Lemont does not have flow monitoring on the North Plant Flare.

Hydrocarbon flare gas from throughout the refinery, except from Coker 2, is routed to the South Refinery FGR system compressor. This FGR system has a capacity to handle [redacted] million cubic feet per day of flare gas. When the FGR system is overwhelmed, flaring occurs, but gases are still recovered up to the capacity of the recovery system. Hydrocarbon flare gas that is not recovered is routed to South Plant Flares, C-2 and C-3. Vent lines for process units in Refinery Blocks 2 and 3 are cross-connected, with water seals segregating the headers for Flares C-2 and C-3. These connections allow both flares to be used in case of a large flaring event. Both flares have three pilots, are steam-assisted, and have similar configurations with a header and knockout drums prior to the flare. Due to configuration of the steam flow meters, the individual steam flows to the C-2 and C-3 flare tips cannot be directly calculated. The South Plant Flares have GE Panametrics flow meters located downstream of knockout drums, before the water seal inside the base of the flare stack. CITGO Lemont has not been able to obtain accurate flow readings since installation of these flow meters, four to five years ago. CITGO Lemont injects steam into the flare headers for winterization and as sweep gas, and suspects a high steam flow rate may be causing problems with the flow measurements.

The Coker 2 Flare, C-4, is steam-assisted and served by a dedicated FGR system. CITGO Lemont does not have flow monitoring on the Coker 2 Flare.

The Alky Flare, C-5, receives flare gas from three unique headers: the acid flare header, the hydrocarbon flare header, and the pump vent header. The acid flare header and pump vent header are routed through an acid relief neutralizer scrubber column which uses potassium hydroxide to neutralize HF in the gas upstream of the flare. The Alky Flare experiences periodic, routine venting from activities at the HF Alkylation Unit such as venting of HF trucks and storage drums. Non-routine events triggering flow to the HF Flare include venting of the feed dryer and defluorinator. The HF Flare is equipped with a GE Panametrics flow meter which has been reliably measuring flare gas flow since installation.

All of CITGO Lemont's flares are subject to NSPS Subpart J, pursuant to the CITGO consent decree with EPA. Due to ULSDHT project tie-ins to the South Plant Flares system, the C-2 and C-3 flares will become subject to requirements under NSPS Subpart Ja. CITGO stated that they are aware of this applicability and are awaiting promulgation of the final rule to determine the method and schedule for compliance. CITGO Lemont does not currently have H_2S CEMS on any flares. None of CITGO Lemont's flares are equipped to analyze flare gas composition via gas chromatography; heating value is determined via periodic sampling. All of CITGO Lemont's flares are equipped with a molecular seal. CITGO provided EPA with the graph shown in Attachment E, illustrating percent of time during which gases were not being flared at the refinery.

13.2 Flare Gas Flow Measurement Issues

On June 11, EPA discussed with Mr. Claude Harmon and Mr. Matt Klickman the issues that CITGO Lemont has been experiencing with the GE Panametrics flow monitors on the South Plant Flares, C-2 and C-3. CITGO provided data to EPA indicating FGR suction pressure and seal pan level for all flares in recent years. The data provided for seal pan alert, which is recorded in binary values, is not actually binary because it is a daily average. This seal pan level indicator data is accurate for C-1; useless for C-2 and C-3, as one indicator is pegged at zero and the other at one; and generally inaccurate for C-4. EPA asked how CITGO Lemont determines whether flaring is occurring at C-2 and C-3. Mr. Harmon stated that operators use cameras to observe flares, and keep a log at each unit when flow is routed to a flare. EPA asked whether CITGO thinks there is a high and/or low threshold of flow at which the GE Panametrics equipment becomes accurate. Mr. Harmon responded no, and that the flow measurements were originally reliable to at least identify flaring events, but in recent years the equipment has registered close to zero flow during significant flaring events.

14. Wastewater Treatment Plant

CITGO Lemont treats process water from the North and South Plants in a common wastewater treatment plant (WWTP). Mr. John Martens led a tour of the WWTP on June 10. Attachment B provides process flow diagrams for the WWTP (p. 15).

The North and South Plants each route process water to separators which facilitate removal of sludge for recycling. Separated water combines with miscellaneous plant wastewater to enter storage tanks which then flow to an induced gas floatation (IGF) unit. Meanwhile, wastewater from sources including the sanitary sewer, cooling tower blowdown, and winterization steam is collected in an equalization tank, followed by an uncovered sedimentation tank, from which oil is skimmed and sludge is collected. After this point, water from the IGF tanks combines with the sedimentation tank supernatant to enter three parallel fine bubble aeration cells. Aeration is followed by two final clarifiers, then the treated water ("polishing") basin. Water from the FCCU wet gas scrubber blowdown flows directly from the FCCU purge treatment unit into the treated water basin. Ultimately, a portion of treated water is recycled for fire water supply, and the remainder discharged to surface water.